APPENDIX B

EXPERIMENTAL RESULTS

Appendix B
Experimental Results

The experimental results are summarized numerically in Table B1. The data are graphically shown in Figures B-1 through B-14 for viscosity, level of delignification, and color and COD in the spent liquor from the oxygen reaction.

Relationship Between TAPPI Viscosity and Intrinsic Viscosity

The Jay, Maine mill uses the 0.5% CED TAPPI viscosity as an indication of pulp strength. The pulp viscosity is related to the change in molecular weight of the carbohydrates after cooking and during bleaching. In this study, both the TAPPI and intrinsic viscosity were measured. The intrinsic viscosity is the preferred method because it is easily correlated with the molecular weight of cellulose and other carbohydrates comprising the pulp. Figure B1 is a plot of 0.5% CED TAPPI viscosity plotted versus intrinsic viscosity. The relationship determined between the TAPPI viscosity (μ, centipoise) and the intrinsic viscosity [η, cm^3/gram] is:

$$m(cp) = 0.0721 * [\boldsymbol{h}, cm^3 / gram] \qquad \text{(B-1)}$$

where $R^2 = 0.825$

The data of Figure B1 show that the softwood pulp viscosity at IP Jay is quite high, even after extended oxygen delignification.

Delignification in the 15-Minute Reactor at Low Caustic Addition

Initial experiments were performed using 1.5% caustic addition based upon pulp. These experiments were performed using well washed pulp having a 15 minute retention time and assuming that little delignification occurred in the 60 minute atmospheric tower. These results are summarized in Figures B2 and B3 and show the effect of consistency (Figure B2) and temperature (Figure B3). These experiments clearly show that low levels of delignification occur when the caustic level in the pulp is low (1.5% based upon pulp) and the temperature in the reactor is low (175 °F). Since these experiments were performed at 10% consistency, the initial concentration of caustic in the pulp mixture is -- by solving equation (1) -- approximately 1.67 grams per liter. This is considerably lower than the measured value of about 3 grams per liter measured in the mill samples (see Table 2).

It is interesting to note that the level of delignification can be improved significantly by raising the temperature (see Figure B3), that is from about 13% at 175 °F to 21% at 205 °F. There is a drop in viscosity as the temperature is raised, but it is not considered significant, from about 1060 cc/gram at 175 °F to 1020 cc/gram at 205 °F. This corresponds to a TAPPI viscosity of 37 centipoise at 175 ^{o}F and 34 centipoise at 205 ^{o}F.

Delignification in the 15-Minute Reactor at High Caustic Addition

The effect of the caustic addition level was investigated on the level of delignification and the reduction in pulp viscosity. This was done by varying the caustic addition level over the range of 2.5%, to 4.5% to encompass the range of caustic concentrations going to the 15 minute reactor at the Androscoggin mill. In the mill application, approximately half of the caustic in the pulp going to the oxygen reactor results from carryover of caustic from the brown stock washers. In these experiments the reaction temperature was kept constant at 175 °F.

These results are summarized in Figure B4. The level of delignification was raised relative to the base case but only reached a level of 19.5% even at the 4.5% caustic addition level. From Figure B4, the percent delignification was only about 16% assuming a NaOH concentration of 3.1 grams per liter in the pulp. A concentration of 3.1 grams per liter at 10% consistency corresponds to about 2.8% total caustic on pulp going to the 15 minute tower.

Thus, it is concluded that the atmospheric tower is leading to a significant amount of delignification and the effect of adding caustic is not nearly as important as raising the temperature; compare the results shown in Figures B3 and B4. It is also interesting to note that as the level of caustic is raised in the pulp, the intrinsic viscosity of the pulp begins to decrease rapidly. These results show the importance of proper control of the level of addition of caustic, and conducting the reaction at the proper temperature.

Two Stage Delignification – 15-Minute Reactor Plus Atmospheric Tower

The effects of temperature and consistency on the rate of oxygen delignification were investigated in a simulation of the two-stage oxygen process being operated at IP-Jay. These experiments were thought to more properly reflect the system at Jay and accounted for the 60-minute reaction time in the atmospheric tower. Experiments were performed assuming that it was feasible to raise the temperature from 175 to 190 °F in both the 15-minute pressurized oxygen reactor and also in the 60 minute atmospheric tower. The results are shown graphically in Figures B5 and B6 for 10% consistency and in Figures B7 and B8 for 12% consistency. Also shown plotted in these figures are the results for operating the 15 minute pressurized reactor at 175 °F. Figures B5 and B7 show the data for the percent delignification while Figures B6 and B8 illustrate the results for the intrinsic viscosity.

Effect of Consistency. Experiments were performed at both 10 and 12% consistency and caustic addition rates of 2.5% and 3.5%. The concentration of caustic in the pulp corresponds to 2.25 and 3.9 grams per liter at 10% consistency for the 2.5% and 3.5% addition rates, respectively. Similarly, the caustic concentration corresponded to 3.4 and 4.8 grams per liter at 12% consistency when the addition rates were 2.5% and 3.5% based upon pulp, respectively. These results clearly show the contribution to the delignification coming from the atmospheric tower and the importance of the raising the temperature in the oxygen delignification process.

Effect of Temperature on Delignification. At a 3% addition rate for caustic, about 3.3 grams per liter in solution, addition of the atmospheric tower to the oxygen delignification process raises the level of delignification from about 16% to 27% when the process is operated at 10% consistency and 175 °F (see Figure B5). Similarly, raising the temperature to 190 °F in both the pressurized reactor and in the tower, the percent delignification can be raised to 37%, again operating at 10% consistency and 3.3 grams per liter caustic concentration (Figure B5).

Similar results are seen when the process is operated at 12% consistency (see Figure 12) where the level of delignification can be raised to 38 or 39% depending upon caustic concentrations. Delignification levels of 40% should be possible if the temperature in the towers could be raised to 200 or 205°F and the operators trained to keep the consistency at 10 to 12% going the oxygen reactor. It is clear from these results that raising the temperature in the reaction is a very important variable.

Pulp Viscosity. At the higher caustic addition rates and temperatures, the intrinsic viscosity is beginning to drop to about 900 to 930 cc/gram depending upon the pulp consistency and the temperature (see Figures B6 and B8). An intrinsic viscosity of 900 to 930 cc/gram corresponds to a 0.5% CED TAPPI viscosity of about 25 to 27 centipoise (Equation 4) which is still quite high. If pulp viscosity ever became an issue, one possible solution would be to add a carbohydrate protector. The most commonly used protector would be addition of magnesium ion as either $MgSO_4$, $MgCO_3$ or $Mg(OH)_2$.

Effect of Mixing

The data contained in Figures B5 and B6 suggest that mixing of oxygen with the pulp in the IP system at Jay, Maine is good and not limiting the reaction.

Table 1 summarizes the mill process data and suggests that the average percent delignification experienced in the softwood mini-oxygen system is about 26.9% and the final pulp intrinsic viscosity is approximately 1100 cc/gram; TAPPI viscosity of about 39 centipoises. This level of delignification is achieved under “average mill conditions” shown in Table 2. Data from Table 2 indicate that the process is being operated at a temperature of 175 °F, measured midway in the oxygen reactor, an alkali concentration corresponding to an addition rate of about 3.1% caustic (about 3.1g/liter) and a consistency of about 9.15%.

The mill results can readily be compared to the results from the experiments shown in Figure B5 that suggest that the delignification rate is about 27% when the reaction is conducted at 175 ^{o}F, 3.1% caustic addition rate and 10% consistency. These results correspond extremely well to the level of delignification being experienced in the mill, also about 27%. The intrinsic viscosity of the pulp obtained in the laboratory was 990 cc/gram (see Figure B6) and corresponds to a TAPPI viscosity of about 32 centipoises. The data for pulp viscosity obtained in the mill is approximately 1100 cc per gram or about 39 TAPPI. The correspondence is not good but can be explained by the effect of conducting the reaction in a small metal reactor where wall effects would be expected to be large. Metal ions contribute to the formation of hydroxyl free radicals that are compared to carbohydrate degradation reactions.

The conclusion drawn from this crude analysis is that in all probability, the oxygen delignification reactions being experienced in the mill are not limited by the mixing in the current high shear mixer. This conclusion is drawn because, in the laboratory reactor, an infinite supply of oxygen is available for the reaction, yet the results are very similar to those obtained in the mill. Rather, these results suggest that the reaction is being controlled by the basic chemistry of the reaction and not by mass transfer effects brought about by insufficient mixing.

Pulp Selectivity

During pulping and bleaching processes designed to remove lignin from the pulp, degradative side reactions occur with the carbohydrates in the pulp that reduce the molecular weight of cellulose and consequently the strength of the pulp. Pulp selectivity is a measure of the relative rates of reaction between the reactant and the carbohydrates and lignin in parallel competitive reactions. Pulp selectivity is defined in several ways, one of which is shown in Figure B9. In this work, the pulp selectivity was defined as the slope of a plot of intrinsic viscosity versus the kappa number. The data show that raising the caustic concentration in the pulp reduces pulp selectivity. An alternative and more appropriate strategy would be to raise the delignification temperature. At 40% delignification, the intrinsic viscosity of the pulp will be approximately 900 cc^3/gram, which corresponds to a TAPPI viscosity of about 25 centipoises.

Lastly, the COD and Color data were converted to Kg per metric ton for use in estimating the change in effluent going to the river from any improvement in oxygen delignification systems in the softwood pulp mill. This was done by using the data shown in Figures B10 and B11 together with equations (2) and (3) respectively, to convert mg per liter into Kg per Tonne for COD and Color. The relationships obtained are:

$$COD\,(Kg\,/\,Tonne) = 0.1058 * \Delta K^{2} + 2.547 * \Delta K \qquad \text{(B-2)}$$

where $R^2 = 0.9733$

$$Color\,(Kg\,/\,Tonne) = 0.2005 * \Delta K^2 + 6.4491 * \Delta K \qquad \text{(B-3)}$$

where $R^2 = 0.9756$

These calculations are summarized in Figures B13 and B14. Equations (B-2) and (B-3) give the results for the COD and color in terms of Kg per metric ton in the spent liquor from the oxygen stage in terms of the change in Kappa No.

COD and Color in Spent Liquor After Oxygen Delignification

The measurements for COD and Color in the spent liquor leaving the oxygen stage are shown plotted in Figures B10, B11, and B12. The data are plotted versus the change in kappa number and essentially correct for carryover of solids from the oxygen washer. In other words, the data shown in Figures B10, B11, and B12 present the results for color and COD over and above that sent to the oxygen reactor as carryover. The mathematical relationships between the COD and Color exiting in the spent liquor are shown on the graphs. Second order polynomials were used to fit the data.

Figure B12 shows that there is a very strong relationship between the amount of COD and Color in the spent liquor from the oxygen stage.

$$Color(mg\,/\,liter) = 2.329 * COD(mg\,/\,liter) + 122.61 \qquad \text{(B-4)}$$

where $R^2 = 0.9956$

Please note the very strong correlation coefficient indicating the relationship between Color and COD. The material that is measured as COD is essentially the same chemical constituents that are measured as Color; namely the dissolved lignin and carbohydrates. The larger the change in kappa number across the oxygen stage, the larger will be the COD in the spent liquor and the larger the concentration of Color. The experimental results for Color and COD clearly confirm the data shown in Figure 3, which was also linear, that was determined for pulp samples going to the oxygen reactor at Jay Maine.

Table B1

Summary of Experimental Data

Stage	Consistency %	Chemical %	%(NaOH) Added	Time (min)	Temp oC	Pressure (psig)	End pH	Initial Conc. g NaOH/l	Residual (g/l)	Kappa No.	% Delignification	ISO brightness %	Intrinsic Viscosity (ml/g)	Tappi Viscosity, centipoise
Brownstock										25.8	-	27.9	1102	40.9
Effect of Consistency	8	1.5 % NaOH	1.5	15	175F	100	11.9	1.3	0.92	22.7	12.0	29.5	1082	39.0
	10	1.5 % NaOH	1.5	15	175F	100	12.0	1.7	1.12	22	14.7	28.8	1057	37.8
	12	1.5 % NaOH	1.5	15	175F	100	12.0	2.0	1.34	21.8	15.5	29.2	1048	37.2
Effect of Temperature	10	1.5 % NaOH	1.5	15	175F	100	12.0	1.7	1.14	22.4	13.2	29.3	1065	35.9
	10	1.5 % NaOH	1.5	15	190F	100	11.9	1.7	1.06	21.4	17.1	29.5	1028	34.2
	10	1.5 % NaOH	1.5	15	205F	100	11.9	1.7	0.98	20.5	20.5	29.9	1017	33.2
Effect of Caustic*	10	2.5 % NaOH	2.5	15	175F	100	12.2	2.8	2.14	21.9	15.1	29.7	1042	29.0
	10	3.5 % NaOH	3.5	15	175F	100	12.3	3.9	3.20	21.2	17.8	29.9	998	35.7
	10	4.5 % NaOH	4.5	15	175F	100	12.5	5.0	4.20	20.9	19.0	30.5	958	31.6
Effect of Time at 10% Consistency	10	2.5% NaOH	2.5	15/60	175F	100/20 to 0	12.3	2.8	2.96	19.2	25.6	29.2	994	31.7
	10	3.5% NaOH	3.5	15/60	175F	100/20 to 0	12.2	3.9	1.99	18.5	28.3	32.1	974	29.4
	10	2.5% NaOH	2.5	15/60	190F	100/20 to 0	12.2	2.8	1.84	16.8	34.9	31.9	959	28.5
	10	3.5% NaOH	3.5	15/60	190F	100/20 to 0	12.3	3.9	2.82	16	38.0	33.6	900	25.9
Effect of Time at 12% Consistency	12	2.5% NaOH	2.5	15/60	175F	100/20 to 0	12.2	3.4	2.45	18.6	27.9	31.4	994	31.5
	12	3.5% NaOH	3.5	15/60	175F	100/20 to 0	12.3	4.8	3.70	17.8	31.0	31.5	930	26.8
	12	2.5% NaOH	2.5	15/60	190F	100/20 to 0	12.2	3.4	2.24	16.4	36.4	32.4	939	27.9
	12	3.5% NaOH	3.5	15/60	190F	100/20 to 0	12.3	4.8	3.37	15.5	39.9	33.6	893	23.7

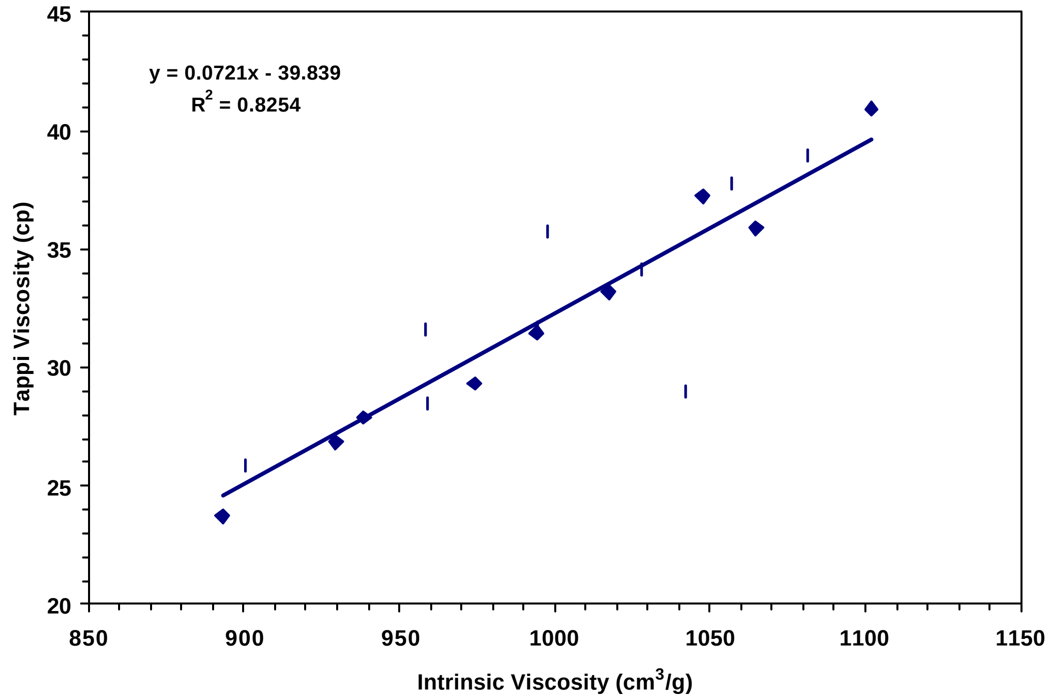

Figure B1
TAPPI (0.5% CED) Viscosity versus Intrinsic Viscosity

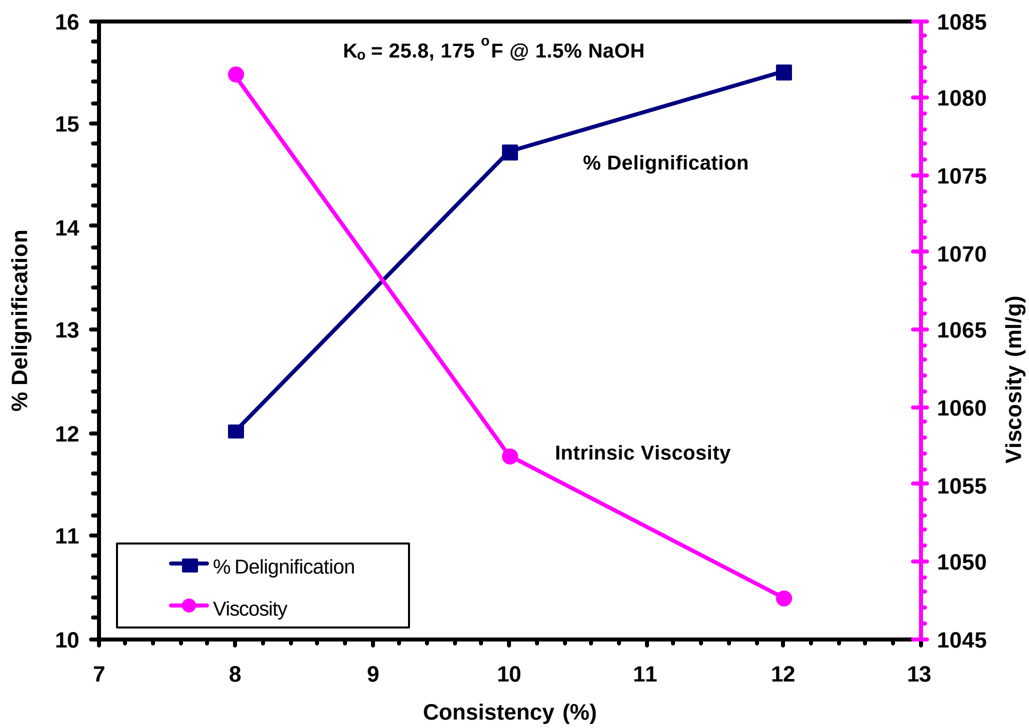

Figure B2.
Effect of Consistency on Percent (%) Delignification and Pulp Viscosity
(15 Minute Reactor)

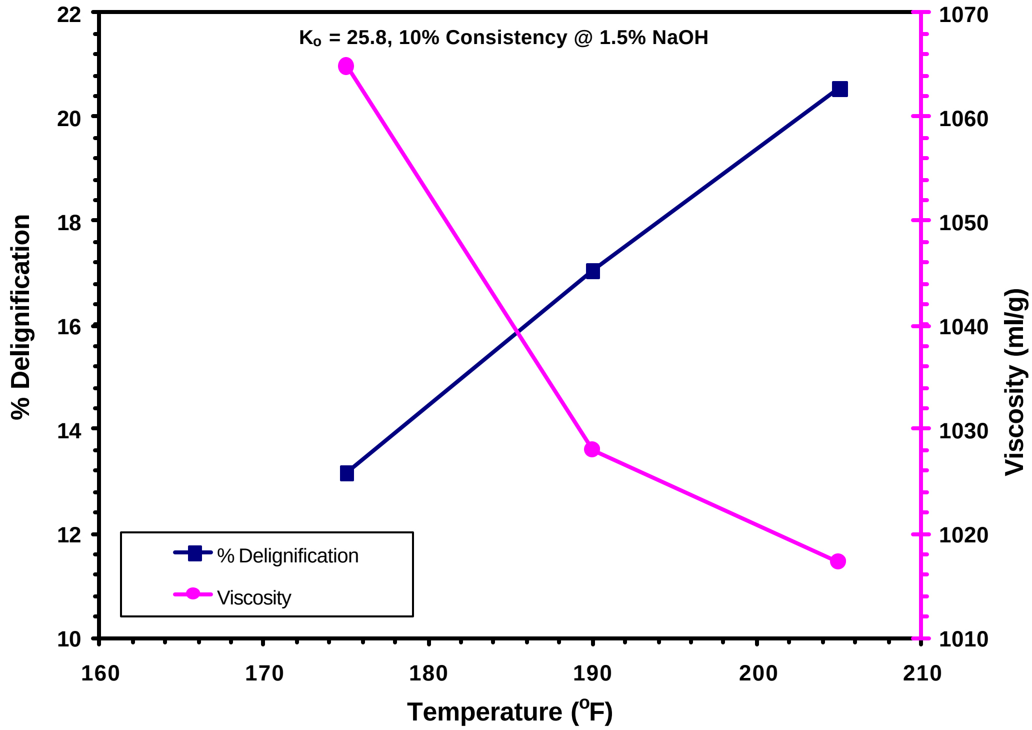

Figure B3
Effect of Temperature on Percent (%) Delignification and Pulp Viscosity
(15 Minute Reactor)

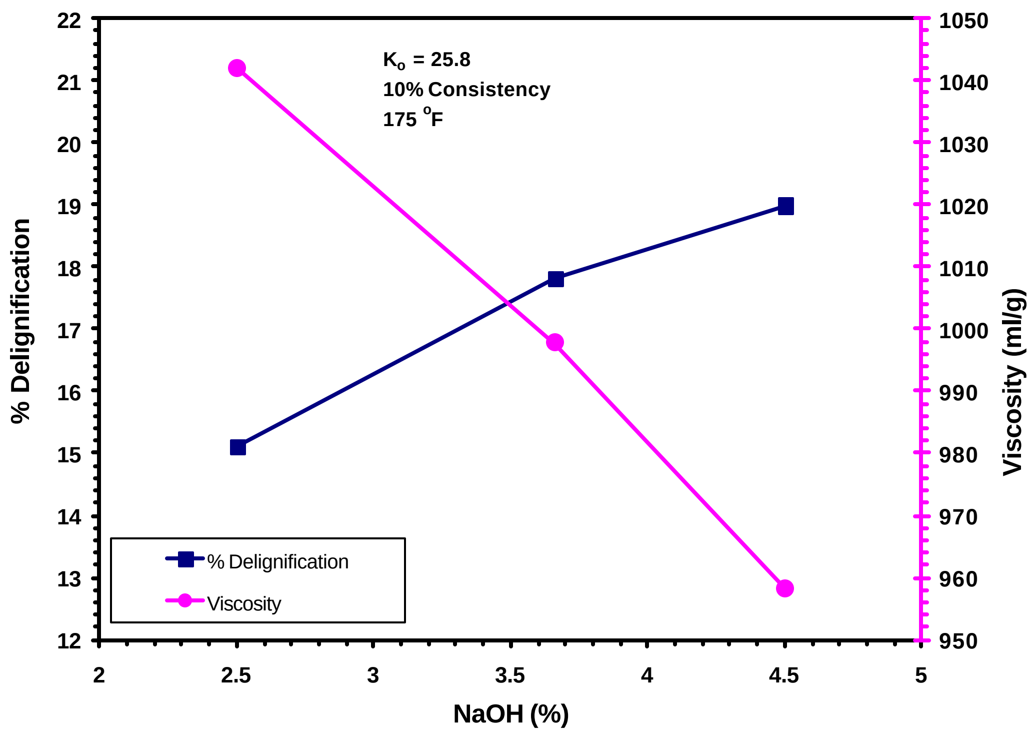

Figure B4
Effect of Caustic (NaOH) Addition on Percent (%) Delignification and Pulp Viscosity
(15 Minutes in Reactor)

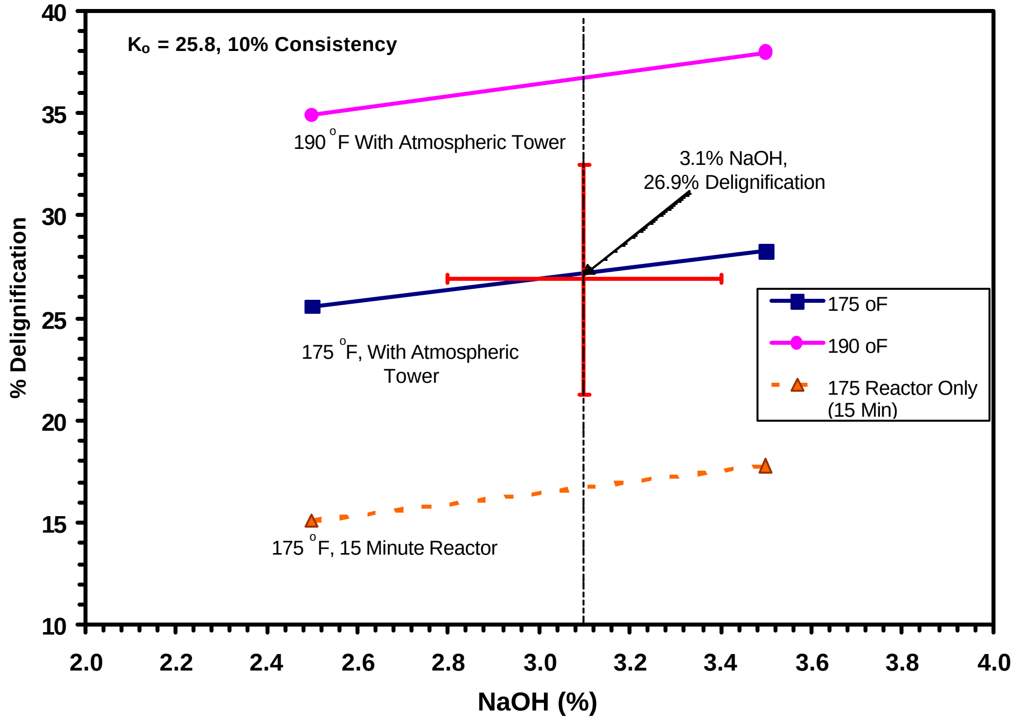

Figure B 5

Effect of Caustic (NaOH) Addition and Temperature on Percent (%) Delignification at 10% Consistency

(15 Minute Reactor plus Atmospheric Tower)

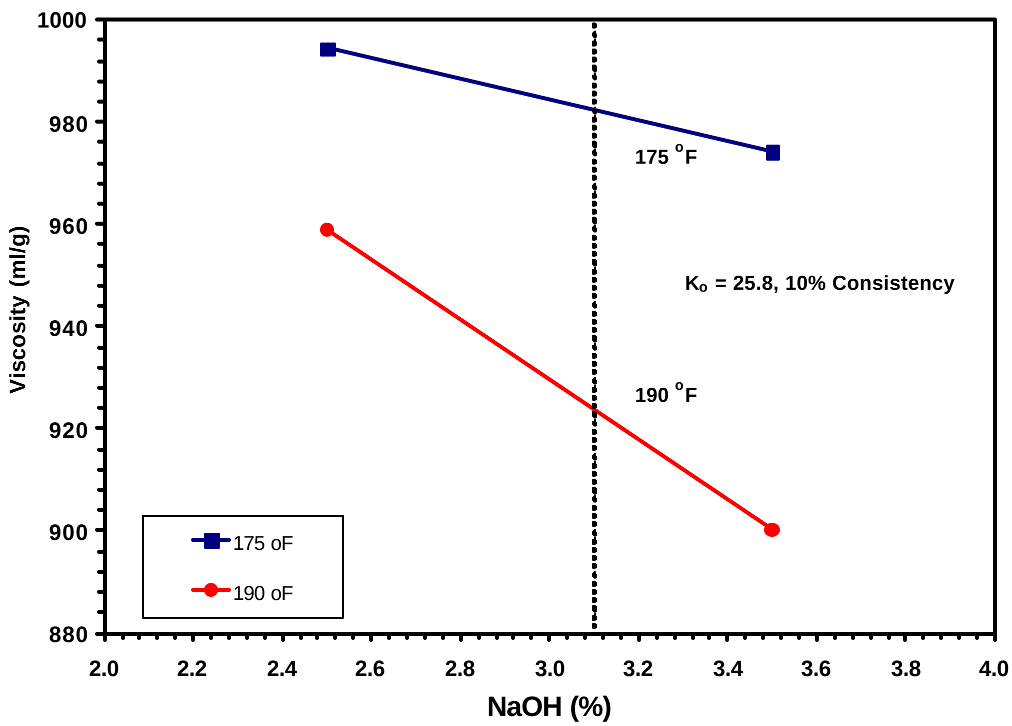

Figure B6

Effect of Caustic (NaOH) Addition and Temperature on Pulp Viscosity at 10% Consistency

(15 Minute Reactor plus Atmospheric Tower)

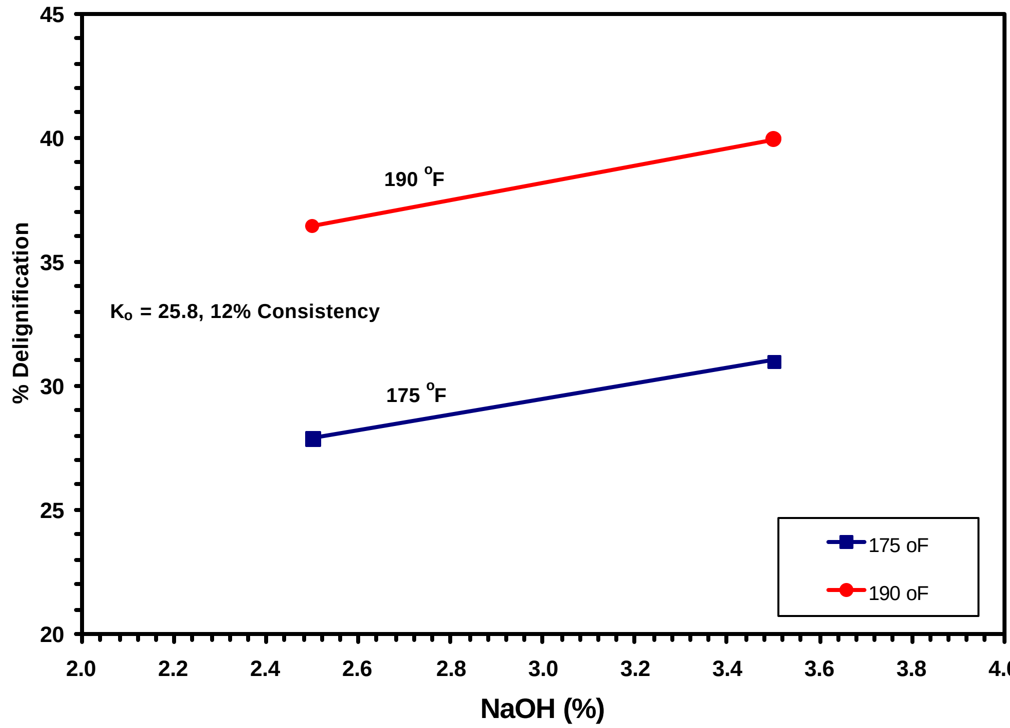

Figure B7
Effect of Caustic (NaOH) Addition on Percent (%) Delignification at 12% Consistency
(15 Minute Reactor Plus Atmospheric Tower)

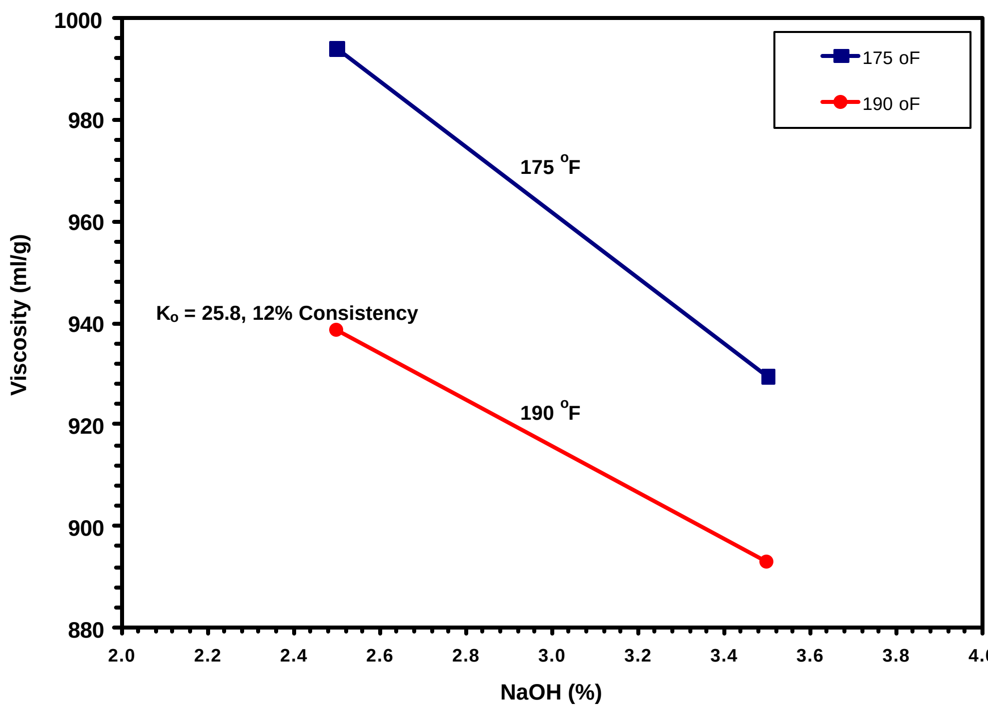

Figure B8
Effect of Caustic (NaOH) Addition and Temperature on Pulp Viscosity at 12% Consistency
(Reactor Plus Atmospheric Tower)

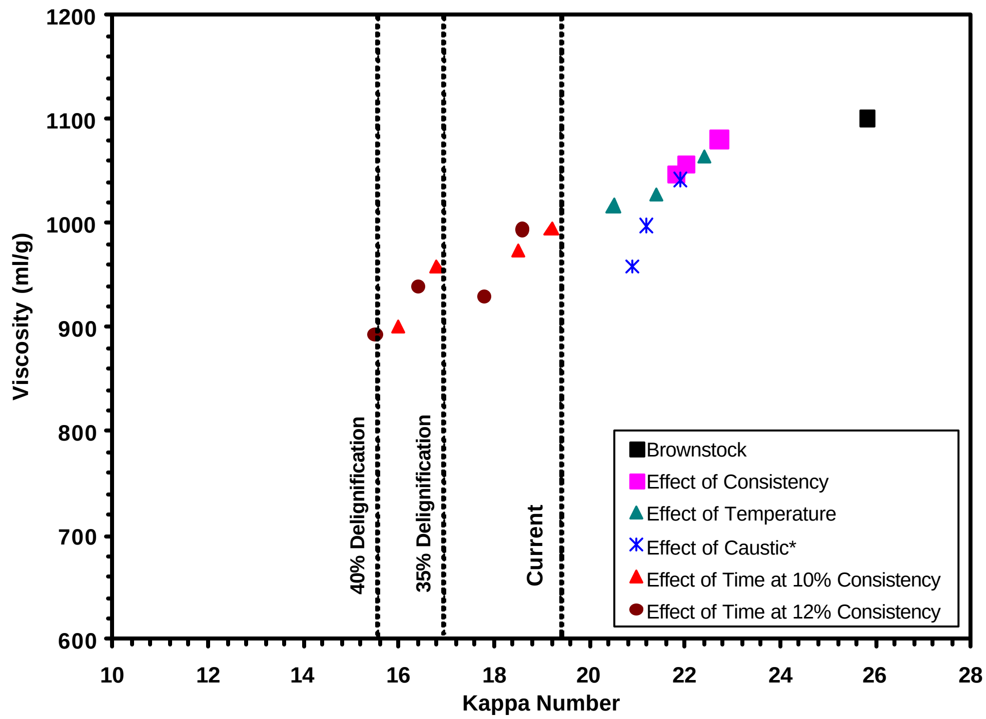

Figure B9

Plot of Pulp Selectivity Defined as Pulp Viscosity Versus Kappa Number

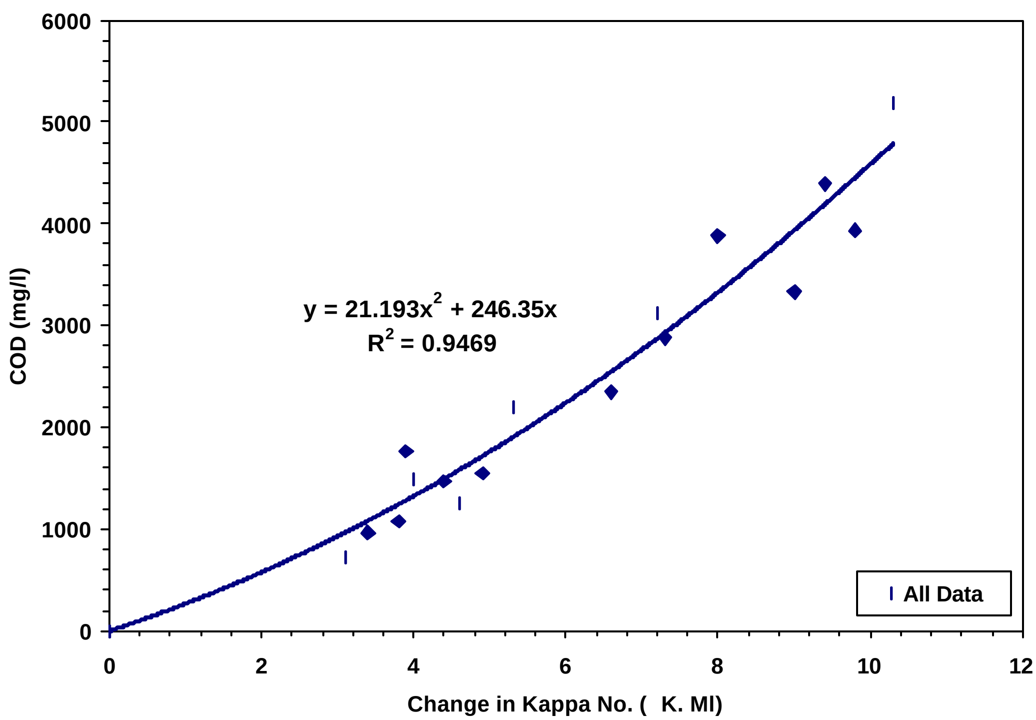

Figure B10
COD (mg/l) in Effluent From Oxygen Stage Versus Drop in Kappa Number

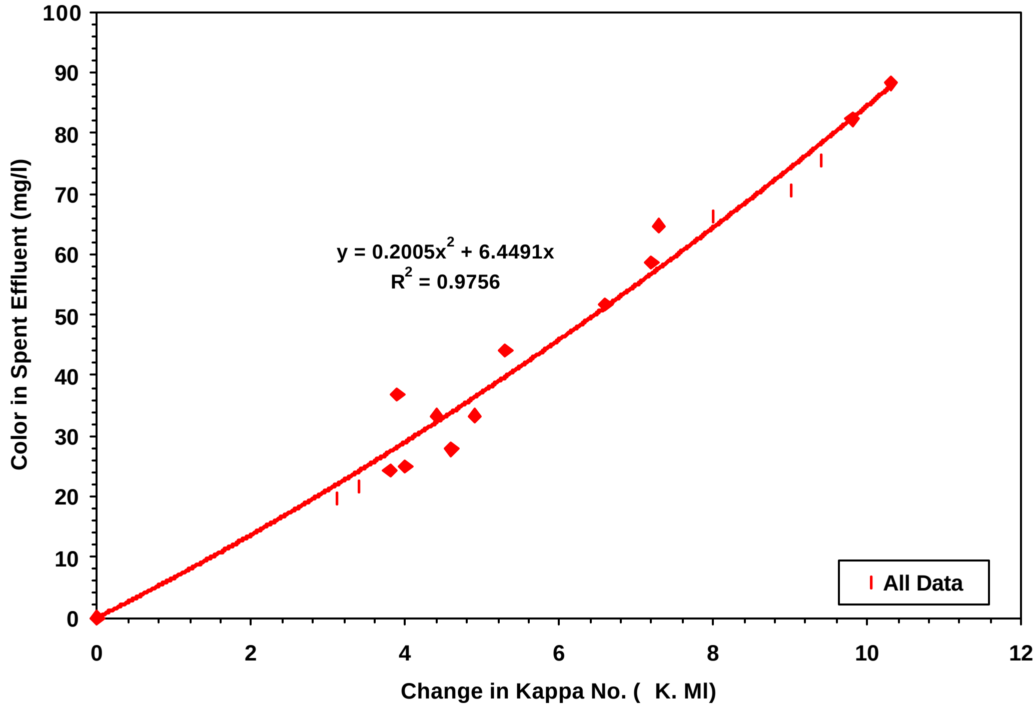

Figure B11
Color in Spent Liquor Versus Change in Kappa Number in the Oxygen Stage

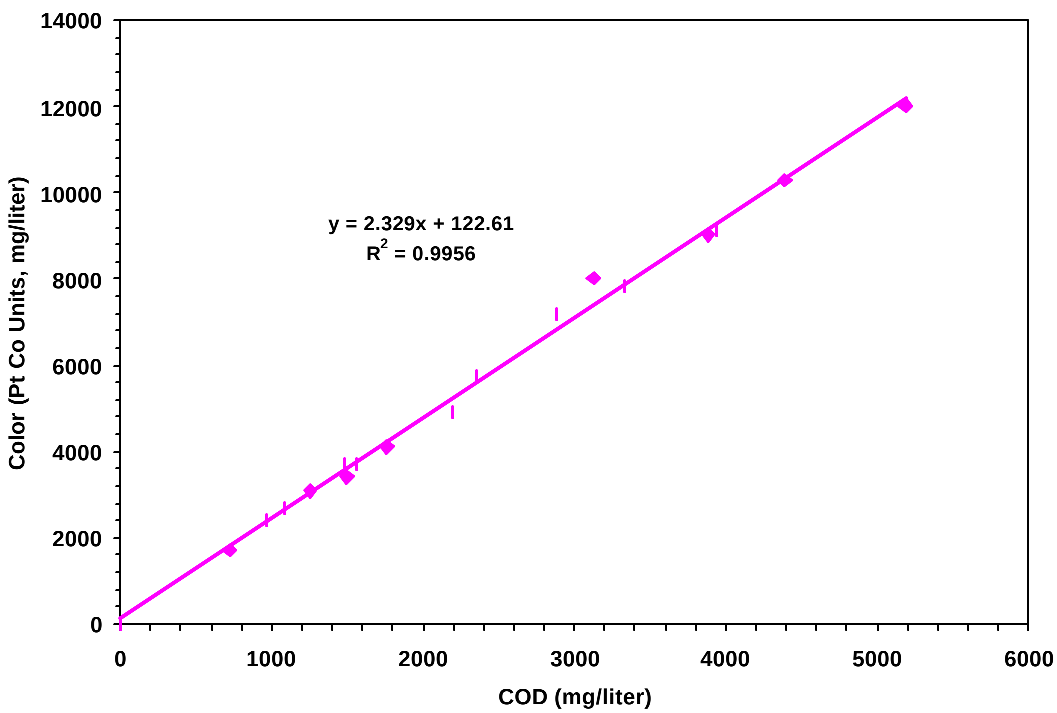

Figure B12
Color Versus COD in Effluent from Oxygen Reactor

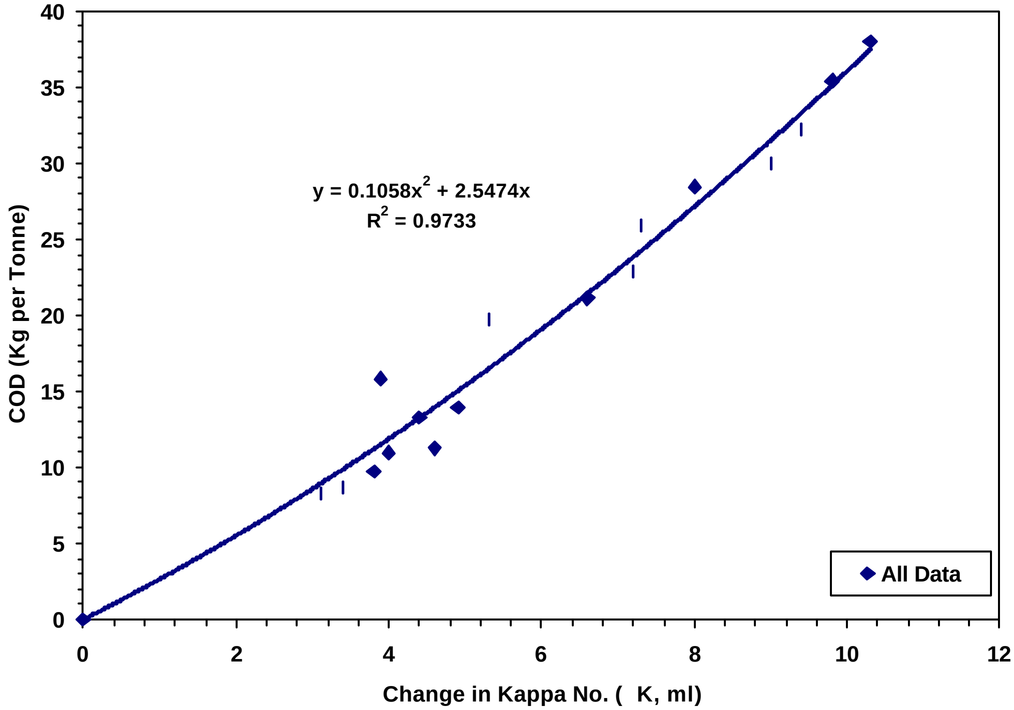

Figure B13
COD in Spent Liquor from Oxygen Stage versus Change in Kappa Number

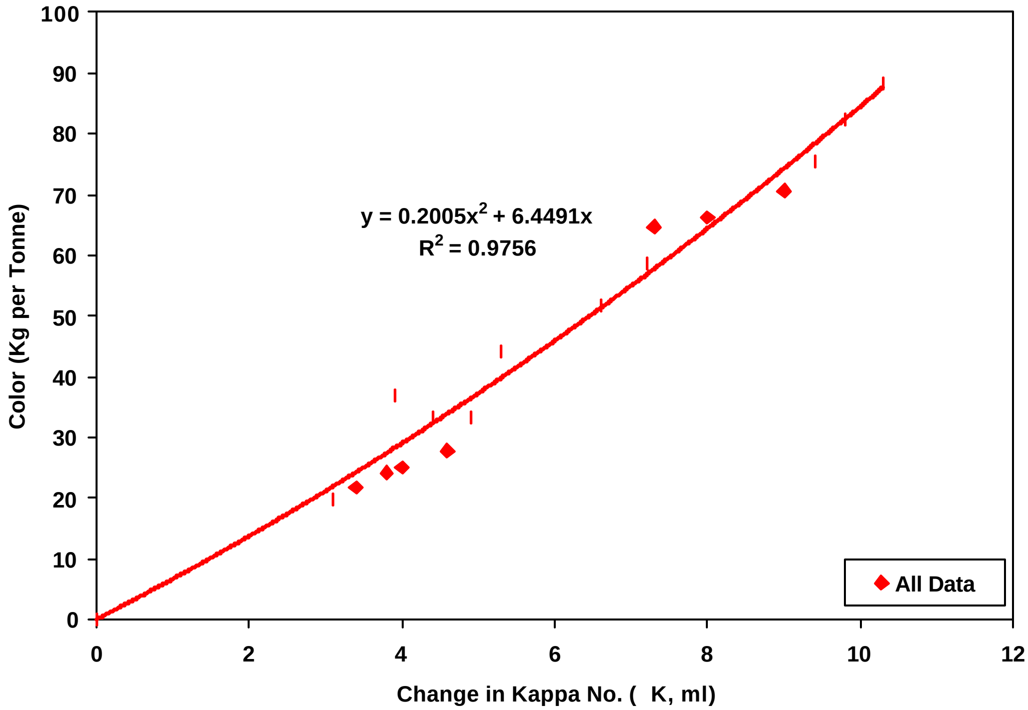

Figure B14
Color (Kg/Tonne) in Spent Liquor from Oxygen Stage versus Change in Kappa No.